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(54) Title: A PEROVSKITE-TYPE FCC NO_x REDUCTION ADDITIVE

(57) Abstract

The NO_x content of FCC regenerator flue gas is reduced using a spinel/perovskite additive which maintains activity during FCC operation in the presence of high levels of sulfur oxides and oxygen. Additionally, a stabilization component may be added to enhance catalytic stability of the additive, and a cracking component may be added under conditions of low reducing agents in the regenerator flue gas.

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1 **A PEROVSKITE-TYPE FCC NOX REDUCTION ADDITIVE**
23 BACKGROUND OF THE INVENTION
4

5 The present invention relates to a method for controlling
6 nitrogen oxides levels in flue gases generated in refinery
7 processing, and specifically in fluid catalytic cracking
8 systems. More particularly, the present invention
9 provides a process for reducing the NO_x content of FCC
10 regenerator flue gas in the presence of sulfur oxides by
11 contacting the flue gas with an additive comprising a
12 perovskite, a spinel, and optionally a stabilization
13 component and a cracking component.

14

15 NO_x Reduction in FCC Regenerators
16

17 Modern hydrocarbon catalytic cracking systems use a moving
18 bed or fluidized bed of a particulate catalyst. Catalytic
19 cracking differs from hydrocracking in that it is carried
20 out in the absence of externally supplied molecular
21 hydrogen. The cracking catalyst is subjected to a
22 continuous cyclic cracking reaction and catalyst
23 regeneration procedure. In a fluidized catalytic cracking
24 (FCC) system, a stream of hydrocarbon feed is contacted
25 with fluidized catalyst particles in a hydrocarbon
26 cracking zone, or reactor, usually at a temperature of
27 about 425° to 600°C. The reactions of hydrocarbons in the
28 hydrocarbon stream at this temperature result in
29 deposition of carbonaceous coke on the catalyst particles.
30 The resulting fluid cracked hydrocarbons and other vapors
31 are separated from the coked catalyst and are withdrawn
32 from the cracking zone. The coked catalyst is stripped of
33 volatiles and cycled to a catalyst regeneration zone. In
34 the catalyst regenerator, the coked catalyst, which
35 usually contains a minor amount of sulfur and nitrogen
36 from the hydrocarbon feed in addition to the carbonaceous
37 coke, is contacted with a gas, such as air, which contains
38 a predetermined concentration of molecular oxygen to burn
39 off a desired portion of the coke from the catalyst and

1 simultaneously to heat the catalyst to the high
2 temperature required for contacting the catalyst with the
3 hydrocarbon stream in the cracking zone. After
4 regeneration, the catalyst is cycled to the cracking zone,
5 where it is used to vaporize the hydrocarbons and to
6 catalyze hydrocarbon cracking. The flue gas formed by
7 combustion of coke in the catalyst regenerator contains
8 steam, oxygen, carbon monoxide, carbon dioxide, and
9 nitrogen. Varying amounts of sulfur oxides and nitrogen
10 oxides may also be present. The flue gas is removed from
11 the regenerator, and may be treated to remove particulates
12 and carbon monoxide from it, after which it is normally
13 passed into the atmosphere. Concerns with control of
14 pollutants in flue gas have resulted in a search for
15 improved methods for controlling such pollutants. In the
16 past, concern has centered on sulfur oxides and carbon
17 monoxide. Nitrogen oxides have more recently become a
18 problem, at least partly because of the use of combustion
19 promoters to burn carbon monoxide.

20
21 In fluidized bed catalytic cracking (FCC), the spent
22 catalyst is reactivated by burning the coke in air.
23 During reactivation (or regeneration) nitrogen oxides,
24 including nitric oxide (NO) and nitrogen dioxide (NO₂) are
25 produced. In the present specification, NO_x will be used
26 herein to represent nitric oxide, and nitrogen dioxide, as
27 well as mixtures containing these gases. NO_x from the FCC
28 catalyst regeneration process become part of the
29 regenerator flue gas. Typical flue gas NO_x concentrations
30 range from about 10 ppmv to about 5000 ppmv and more
31 commonly from about 50 ppmv to about 500 ppmv. Because
32 NO_x is an important contributor to general air pollution
33 problems, refineries may treat their FCC flue gas to
34 reduce their overall NO_x emissions. U.S. Patent No.
35 3,900,554 describes a homogeneous gas phase reduction of
36 NO_x with ammonia at a temperature range of 870° to 1100°C.
37 To treat FCC flue gas at these temperatures, the flue gas

1 leaving the regenerator is first mixed with ammonia and
2 then passed through a CO boiler where temperatures are
3 high enough to allow the gas phase reduction to occur.
4 Typical NO_x reductions are on the order of 40 to 70% with
5 this technology. However if the FCC unit does not have a
6 CO boiler or if stricter air quality standards are
7 imposed, alternate technologies need to be considered.
8 U.S. Patent No. 3,279,884 describes selective catalytic
9 reduction where NO_x is reduced by ammonia over vanadium
10 oxide, molybdenum oxide, or tungsten oxide at a
11 temperature range of 150°C to 400°C. While the "selective
12 catalytic reduction" system is capable of reducing NO_x to
13 low levels, it is also more expensive to build and
14 operate.

15

16 An alternative solution, which eliminates the need for a
17 costly selective catalytic reduction system, entails the
18 use of a NO_x reducing additive added to the catalyst
19 inventory. Several metals-containing catalysts, including
20 the zinc-containing catalyst of U.S. Patent No. 5,002,654
21 and the antimony-containing catalyst of U.S. Patent No.
22 4,988,432 when added to the FCC cracking catalyst, have
23 been proposed for reducing the NO_x content in catalytic
24 cracking regenerator flue gas. U.S. Patent No. 4,988,432
25 is directed to reducing the CO and NO_x content of
26 regenerator flue gas in the catalytic cracking of a heavy
27 hydrocarbon feed containing nickel and nitrogen compounds
28 by adding to the inventory of circulating particulate
29 solids a CO combustion promoter and a separate particulate
30 additive containing antimony to reduce the production of
31 NO_x.

32

33 Rare earth metals have also been found to be useful for
34 reducing the NO_x content of gaseous streams. For example,
35 U.S. Patent No. 3,865,923 teaches a process using a
36 copper/rare earth/manganese oxide having a perovskite type
37 crystal structure for reducing the hydrocarbon, carbon

1 monoxide and nitrogen oxide content of engine exhaust gas.
2 U.S. Patent No. 3,914,389 describes a process for
3 preparing a lanthanum copper manganese oxide compound
4 which is taught as having oxidation activity and thermal
5 stability for use as an auto exhaust oxidation catalyst.
6 U.S. Patent No. 3,929,670 describes a catalyst consisting
7 essentially of lanthanum, a lanthanide, copper, and an
8 element selected from lithium, aluminum, titanium,
9 vanadium, chromium, manganese, iron, cobalt, nickel, zinc,
10 gallium, zirconium, tin, molybdenum, and tungsten.

11
12 Zeolites have been disclosed as NO_x reduction catalysts
13 for furnace flue gas application in U.S. Patent No.
14 4,798,513 and U.S. Patent No. 4,973,399. U.S. Patent No.
15 4,798,813 describes a titania/zeolite catalyst with the
16 zeolite having 0.01-20 % by weight copper supported
17 thereon for the reduction of nitrogen oxides in oxidation
18 furnace flue gas. This patent is directed to the problem
19 of catalyst poisons such as arsenic, selenium, and
20 tellurium, which are taught to be partially excluded from
21 the catalytic copper by the small zeolite pores in which
22 some of the copper is located. U.S. Patent No. 4,973,399
23 teaches using a zeolite having a pore size greater than 5
24 Angstroms and containing rare earth metal compounds and
25 0.25 moles CuO per mole of zeolitic alumina supported in a
26 titania or zirconia matrix. U.S. Patent No. 5,085,762
27 discloses a process for reducing NO_x and carbon monoxide
28 emissions from a catalytic cracking process using copper-
29 containing additive particles of a crystalline zeolite
30 labeled "MCM-22".

31
32 U.S. Patent No. 4,963,520 discloses a metal-containing
33 spinel composition containing a sulfur oxidation promoter
34 and a metal promoter for reducing a metal sulfate. U.S.
35 Patent No. 4,790,982 discloses a process for using the
36 composition of '520 for reducing the SO_x and/or the NO_x
37 content of a gas. The spinel of '520 and '982 include a

1 first metal and a second metal having a valence higher
2 than that of the first metal. Group IB metals, Group IIB
3 metal, Group VIA metal, the rare earth metals, the
4 platinum group metals and mixtures thereof are taught as
5 being effective as the sulfur oxidation promoters. The
6 metals iron, nickel, titanium, chromium, manganese,
7 cobalt, germanium, tin, bismuth, molybdenum, antimony, and
8 vanadium are disclosed as effective promoters for the
9 reduction of the first metal sulfate.

10

11 The problem of NO_x reduction catalyst stability in FCC
12 service is partially addressed in U.S. Patent No.
13 5,037,538, which teaches a process for reducing the NO_x
14 content of regenerator flue gas using a NO_x reduction
15 catalyst which has an extended residence time in the
16 fluidized catalytic cracker regenerator relative to the
17 residence time of the FCC cracking catalyst.

18

19 However, none of the art cited above adequately addresses
20 the problem of the stability and activity of the NO_x
21 reduction catalyst in fluid catalytic cracking operations.
22 In order to be effective in commercial operation, the NO_x
23 reduction catalyst must maintain activity while being
24 subjected to repeated redox cycles in the severe
25 hydrothermal environment of the FCC reactor unit and the
26 FCC regenerator unit. Furthermore, in conventional NO_x
27 reduction processes for FCC regenerator flue gas, sulfur
28 oxides and excess oxygen significantly reduce catalyst
29 effectiveness, and an insufficient amount of a reducing
30 agent reduces NO_x reduction rates. The process and
31 additive of the present invention overcome these
32 deficiencies.

33

SUMMARY OF THE INVENTION

35

36 The essence of the present invention resides in the
37 discovery of an additive which, when used at FCC

1 regenerator conditions, reduces the NO_x content of FCC
2 flue gas while maintaining high activity and stability.
3 Furthermore, the additive maintains high activity and
4 stability in the presence of a flue gas containing high
5 levels of sulfur oxides and oxygen, and low levels of a
6 reducing agent. In accordance with the present invention,
7 a process is provided for reducing the NO_x content of FCC
8 regenerator flue gas comprising contacting said flue gas
9 at FCC regenerator conditions with an NO_x reducing
10 effective amount of an additive comprising a perovskite
11 containing at least one transition metal; a spinel
12 containing at least one Group IIA element and at least one
13 Group IIIA element; and at most about 10 weight percent of
14 a stabilization component comprising an element or
15 compound thereof selected from the group consisting of
16 copper, zinc and mixtures thereof. The additive may also
17 contain a cracking component. A catalytic material known
18 to form carbonaceous coke at the conditions of the FCC
19 reactor may be included as the cracking component in the
20 additive.

21
22 In another embodiment, a process is provided for reducing
23 the NO_x content of sulfur-containing FCC regenerator flue
24 gas, said process comprising cracking hydrocarbons in the
25 absence of externally supplied molecular hydrogen in a
26 cracking system employing an inventory of circulating
27 particulate solids including cracking catalyst particles,
28 said inventory being cycled between a cracking zone and a
29 catalyst regeneration zone, wherein said hydrocarbons are
30 cracked in contact with said catalyst particles and coke
31 is formed on said catalyst particles at cracking
32 conditions in said cracking zone, and flue gas is formed
33 by burning said coke off said catalyst particles with
34 oxygen or a molecular oxygen-containing gas at
35 regeneration conditions in said regeneration zone, and
36 said flue gas is vented from said regeneration zone,
37 wherein said process comprises adding to said inventory of

1 circulating particulate solids an NO_x reducing effective
2 amount of an additive comprising a perovskite containing a
3 transition metal, a spinel containing at least one Group
4 IIA element and at least one Group IIIA element; and at
5 most about 10 weight percent of a stabilization component
6 comprising an element or compound thereof selected from
7 the group consisting of copper, zinc and mixtures thereof.
8

9 Further to the invention, an NO_x reduction additive is
10 provided, said additive comprising a perovskite containing
11 at least one transition metal; a spinel containing at
12 least one Group IIA element and at least one Group IIIA
13 element; and at most about 10 weight percent of a
14 stabilization component comprising an element or compound
15 thereof selected from the group consisting of copper, zinc
16 and mixtures thereof. In a separate embodiment, the
17 additive may optionally contain a cracking component.
18

19 Among other factors, the present invention is based on the
20 discovery of a NO_x reduction additive which maintains high
21 activity in severe NO_x reduction service, such as, for
22 example, in an FCC. In contrast to conventional additives
23 for NO_x control, the present additive maintains high
24 activity during repeated redox cycling in the FCC reactor
25 and the FCC regenerator. The additive also maintains high
26 activity in the presence of sulfur oxides, in the presence
27 of excess oxygen, and in an environment of low levels of a
28 reducing agent.
29

30 The full scope of the present invention will be apparent
31 to those familiar with reducing the NO_x content of
32 combustion flue gas from the following detailed
33 description of the principle features of the invention and
34 from the examples which accompany the description.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, "activity" is a measure of the ability of the additive to remove NO_x from the flue gas. As the activity of the additive increases, the NO_x content of the flue gas decreases, at constant regenerator conditions. As used herein, "stability" is a measure of the ability of the additive to maintain constant activity over time when used in the present process.

PEROVSKITE

As noted above, one of the critical constituents of the present NO_x reduction additive is a perovskite containing at least one transition element selected from Groups VIB, VIIIB, VIII, IB, and IIB of the Periodic Table. Preferably, the transition metal component is selected from the group consisting of chromium, manganese, iron, cobalt, nickel, copper, and zinc.

The perovskite may also comprise at least one component selected from the group consisting of Group IA, Group IIA, and Group IIIB elements, wherein the Group IIIB elements are more preferred. Included in the Group IIIB elements are the rare earth elements, having atomic numbers from 57 to 71 inclusive. In the most preferred embodiment, the perovskite component has the general formula LnCu_xMn_{1-x}O₃, where "Ln" is a rare earth element or mixture of rare earth elements, and where x has a value of at most about 0.6.

The notation used herein to represent elements (i.e. Groups IA, IIA, and IIIB) is taken from the PERIODIC TABLE OF THE ELEMENTS located in the inside front cover of R.H. Perry and C.H. Chilton, *Chemical Engineers' Handbook*, Fifth Edition, McGraw-Hill Book Company, 1973.

1 The perovskite can be synthesized by a variety of routes,
2 including heating finely ground intimate mixtures of
3 active sources of the perovskite at a temperature in the
4 range from about 500°C to 1300°C, and more preferably in
5 the range of from about 600°C to about 900°C. Typical
6 active sources of the perovskite includes carbonates,
7 hydroxides, nitrates, oxalates, and/or oxides of the
8 transition metals and of the Groups IA, IIA, and IIIB
9 elements. When perovskites are prepared using a mixture
10 of rare earth elements and this rare earth mixture
11 contains cerium, the stoichiometry of the composition may
12 require adjustment to account for reactions between cerium
13 and other rare earth elements forming oxides which have
14 non-perovskite structures.

15

16 Additionally, the stoichiometry of the active sources are
17 preferably controlled during preparation of the perovskite
18 so that most, if not all, of the transition metal element
19 is consumed during the reaction forming the perovskite.
20 Otherwise the excess transition metal may act to
21 dramatically decrease the life of the additive. Thus, it
22 is preferred that the active sources of the perovskite be
23 combined such that the perovskite contains a Group IA,
24 IIA, and/or IIIB combination to transition metal atomic
25 ratio equal to or greater than about one (1).

26

27 As used herein, the term "perovskite" represents a metal
28 oxide having either an ideal or "defect" perovskite-type
29 crystal structure. The crystal structure of an ideal
30 perovskite is cubic, but frequently crystallographic
31 distortions can greatly reduce the symmetry. Ideal
32 perovskites have the empirical formula, ABO_3 , where the A
33 cation occupies a cubic close packed site (thus is
34 coordinated to 12 oxygen atoms), while the B cation
35 occupies an octahedral hole in the close packed structure.

36

37

In many perovskite-type compounds (also referred to as "defect perovskites") the sum of the valences of the A and B cations may be less than 6. The net result is that the oxygen-sublattice contains a large number of vacancies or defects, which may or may not be ordered. If the oxygen vacancies are ordered, the crystal structure as well as the stoichiometry can be dramatically altered from that of the ideal perovskite. See, for example, M.A. Beno, et. al., *Appl. Phys. Lett.* 51, 57, 1987. Defect oxide forms of perovskites, alone or in combination with defect oxide spinels, have been disclosed as NO_x reduction catalysts in U.S. Patent No. 5,093,301.

13

14 The following references provide additional details on the
15 composition and structure of perovskites: U.S. Patent No.
16 5,110,782, issued 5/5/92 to H. Hirono, et.al.; C. Palache,
17 et. al., "The System of Mineralogy: Seventh Edition", Vol.
18 I, John Wiley & Sons, Inc., 1944, p. 730f; W.W.
19 Porterfield, "Inorganic Chemistry", Addison-Wesley
20 Publishing Company, 1984, p. 109,110.

21

SPINEL

23

24 The NO_x reduction additive also comprises a spinel
25 containing at least one Group IIA element and at least one
26 Group IIIA element. The preferred Group IIA element is
27 magnesium and the preferred Group IIIA element is
28 aluminum. It is more preferred that the atomic ratio of
29 the Group IIA element(s) to the Group IIIA element(s) in
30 the NO_x reduction additive be in the range from about 0.25
31 to about 2.5.

32

33 The spinel component of the present process may be
34 prepared from active sources of Group IIA and Group IIIA
35 elements, using methods known to the art, for example, in
36 U.S. Patent No. 4,904,627, the disclosure of which is
37 included herein by reference. However, reasonable care

1 must be taken to prevent damage to one of the components
2 of the additive during preparation of another component of
3 the solid. For example, one skilled in the art of
4 perovskite materials and of zeolitic cracking catalysts
5 will appreciate the detrimental result of contacting these
6 materials with solutions having a low, i.e. acidic, pH.
7 Thus, during the preparation of the additive, it is
8 important to avoid a condition in which the pH is
9 sufficiently low to adversely affect the structural
10 integrity of the perovskite component or optionally the
11 cracking component. Accordingly, it is preferred that the
12 pH of the reaction mixture used in preparing the spinel
13 component in the presence of the perovskite component be
14 at least 3.5, and preferably at least 4.0.

15

16 It is also preferred that the spinel and the perovskite be
17 intimately mixed in the additive particle. This can be
18 achieved in a number of ways. Non-limiting examples
19 include, forming either a slurry or a gel mixture
20 containing a spinel and/or spinel precursor and a
21 perovskite and/or perovskite precursor. The cracking
22 component may also be added. The slurry or gel may be
23 dried and calcined before use. The method of drying the
24 slurry or gel is not critical, and may include either
25 drying in a static bed or by spray drying. These methods
26 are well known in the art. The calcining step involves
27 heating the dried gel in air at a temperature between
28 about 500°C and about 900°C, and preferably between about
29 600°C and about 750°C. The solids prepared in this manner
30 may be added to the inventory of circulating particulate
31 solids of the FCC.

32

33 The term "spinel" refers in general to a class of mixed
34 metal oxides having a common crystallographic structure.
35 The spinel structure is a cubic close-packed array of
36 oxide ions having cations occupying 1/8th of the
37 tetrahedral sites and 1/2 of the octahedral sites in the

1 array. Typically, the crystallographic unit cell of the
2 spinel structure contains 32 oxygen atoms. The structure
3 can be symbolized by $D[E_2]O_4$, in which the E ions (enclosed
4 in brackets) are in octahedral coordination. In the
5 naturally-occurring magnesia alumina spinel ($MgAl_2O_4$), Mg^{2+}
6 ions occupy the tetrahedral sites and Al^{3+} the octahedral
7 sites. Many other mixed metal oxides are known to assume
8 the spinel structure or a variation of it. One variation
9 is the inverse spinel structure, having a structure
10 symbolized by $E[DE]O_4$, in which the D cations are in
11 octahedral sites, half the E cations are also in
12 octahedral sites and half in tetrahedral sites. The
13 following references provide additional details on the
14 composition and structure of spinels: U.S. Patent No.
15 5,108,979, C.S. Hurlbut, "Dana's Manual of Mineralogy",
16 John Wiley & Sons, Inc., 1971, p. 292-5; W.W. Porterfield,
17 "Inorganic Chemistry", Addison-Wesley Publishing Company,
18 1984, p. 109,110; and F.A. Cotton and G.Wilkinson,
19 "Advanced Inorganic Chemistry, Fifth Edition", John Wiley
20 & Sons, 1988, p. 9.

21

STABILIZATION COMPONENT

22

23
24 To improve long term reaction stability of the additive, a
25 stabilization component comprising an element or compound
26 thereof selected from the group consisting of copper, zinc
27 and mixtures thereof may be included with the additive.
28 The stabilization component is a distinct component of the
29 additive, preferably in intimate mixture with the spinel
30 and the perovskite.

31

CRACKING COMPONENT

32

33
34 The NO_x reduction additive particle may also optionally
35 include, in addition to the spinel and perovskite
36 components and any stabilization components, at least one
37 cracking component. Catalytic materials known to have

1 cracking activity at the conditions of the FCC reactor are
2 suitable as cracking components in the present process.

3

4 **ADDITIVE**

5

6

7 The additive of the present process comprises from about 1
8 to about 40 weight percent, preferably from about 5 to
9 about 35 weight percent, more preferably from about 10 and
10 about 30 weight percent of the perovskite; at most about
11 10 weight percent, preferably between about 0.1 to about 5
12 weight percent, more preferably from about 0.5 to about 5
13 weight percent of the stabilization component; and the
14 spinel to make 100 weight percent.

15

16 The composition of the additive, as described herein, is
17 stated in terms of weight percent of the additive, wherein
18 weight percent of a component is equal to $100 * \text{weight of}$
19 the component/weight of the calcined additive. The
20 stabilization component weight percent is given on a
21 stabilization metal basis.

22

23 **NOX REDUCTION IN THE FCC PROCESS**

24

25 In order to fully appreciate the basis for limiting the
26 present invention to embodiments depending from the
27 features of the invention, it is useful to identify
28 features of the NOx reduction additive which are thought
29 to contribute to the NOx reduction properties of the
30 additive. Although a description is helpful to explain
31 the mechanism which is believed to be involved in the
32 present invention, it is theoretical and is offered only
33 to assist in understanding the scope of the present
34 invention and the advantageous results which can be
35 achieved by the present invention. Therefore, it is not
36 intended that the present invention should be limited by

1 the theory of its operation, but rather by the resulting
2 features.

3

4 It is advantageous to put the process of this invention in
5 the context of the overall FCC process. The fluid
6 catalytic cracking (FCC) process is well known, and is
7 described, for example, in Kirk-Othmer: *Encyclopedia of*
8 *Chemical Technology*, Vol 17, John Wiley & Sons: New York,
9 3rd Edition, 1982, p.206f. U.S. Patent Nos. 4,309,309;
10 5,002,653 and 5,098,554, the disclosures of which are
11 incorporated herein by reference, also describe the FCC
12 process, including FCC regenerator conditions. The
13 present process for reducing the NO_x content of FCC
14 regenerator flue gas comprises cracking hydrocarbons in
15 the absence of externally supplied molecular hydrogen in a
16 cracking system employing an inventory of circulating
17 particulate solids, including cracking catalyst particles.
18 The cracking catalyst particles which may be used are well
19 known in the art. In general, they are molecular sieves
20 having cracking activity dispersed in a matrix.
21 Illustrative examples include aluminosilicate zeolites,
22 such as zeolite Y, rare earth exchanged zeolite Y,
23 ultrastable zeolite Y, calcium-exchanged zeolite Y; medium
24 pore zeolites such as ZSM-5; medium pore and large pore
25 silicoaluminophosphates; and amorphous materials such as
26 acid exchanged clay, and amorphous aluminosilicate.

27

28 The inventory of circulating particulate solids is cycled
29 between a cracking zone and a catalyst regeneration zone.
30 Hydrocarbons are contacted with cracking catalyst
31 particles in the cracking zone. A suitable weight ratio
32 of catalyst to total oil charge is about 4:1 to about
33 25:1, preferably about 6:1 to about 10:1. The fresh
34 hydrocarbon feed is generally preheated to a temperature
35 of about 600°F to about 700°F, but is generally not
36 vaporized during preheat and the additional heat required

1 to achieve the desired reactor temperature is imparted by
2 hot, regenerated catalyst.

3

4 The reaction temperature in the reaction zone is at least
5 about 900°F. The upper limit can be about 1100°F or more.
6 The preferred temperature range is about 950°F to about
7 1050°F. The reaction total pressure can vary widely and
8 can be, for example, about 5 to about 50 psig, or
9 preferably, about 20 to about 30 psig. The maximum
10 residence time is about 5 seconds, and for most charge
11 stocks the residence time will be about 0.5 to about 2.5
12 seconds or less. The length to diameter ratio of the
13 reactor can vary widely, but the reactor should be
14 elongated to provide a high linear velocity, such as about
15 25 to about 75 feet per second; and to this end a length
16 to diameter ratio above about 20 to about 25 is suitable.
17 The reactor can have a uniform diameter or can be provided
18 with a continuous taper or a stepwise increase in diameter
19 along the reaction path to maintain a nearly constant
20 velocity along the flow path. The amount of diluent can
21 vary depending upon the ratio of hydrocarbon to diluent
22 desired for control purposes. If steam is the diluent
23 employed, a typical amount to be charged can be 1-10
24 percent by weight, based on hydrocarbon charge. A
25 suitable but non-limiting proportion of diluent gas, such
26 as steam or nitrogen, to fresh hydrocarbon feed can be
27 about 0.5 to about 10 percent by weight.

28

29 Coke is formed on said catalyst particles at cracking
30 conditions in said cracking zone, and flue gas is formed
31 by burning coke off said catalyst particles with a
32 regeneration gas or gas mixture at regeneration conditions
33 in a regeneration zone, and said flue gas is vented from
34 said regeneration zone. The regeneration gas or gas
35 mixture employed must have an appropriate free oxygen
36 (molecular oxygen) content. Normally, air is quite
37 suitable for use in supplying free oxygen, but use of air

1 is not essential. For example, pure oxygen or oxygen-
2 enriched air can also be used, if desired. Conventional
3 gases used in commercial FCC operations, such as free
4 nitrogen (molecular nitrogen), carbon dioxide, steam, and
5 the like, are suitable for use as fluidizing and
6 entrainment gases.

7

8 In general, regeneration conditions employed include a
9 combination of temperature and pressure sufficient to
10 permit the specified degree of coke combustion, carbon
11 monoxide combustion and nitrogen oxides reduction to take
12 place, in the manner discussed herein. Temperatures of
13 1000°F to 1500°F (540°C to 815°C) are normally quite
14 suitable. Temperatures of 1100°F to 1350°F (590°C to
15 730°C) are preferred. The rates of flow of regeneration
16 gas, entrainment gases and catalyst particles through the
17 system are maintained at levels which provide a dense-
18 phase fluidized bed of catalyst. Fluid bed operation can
19 be accomplished in a conventional manner by maintaining
20 upward superficial gas velocities appropriate to the size
21 and density of catalyst particles undergoing regeneration
22 and by maintaining catalyst introduction and withdrawal
23 rates at proper levels. The operating pressure is usually
24 not particularly critical. Pressures of 1-10 atmospheres
25 are generally quite suitable. Pressures of 2-5
26 atmospheres are preferred.

27

28 The NO_x additive may be combined uniformly with all of the
29 particles in the inventory of circulating particulate
30 solids in the present FCC process. Alternatively, the
31 inventory of circulating particulate solids in the present
32 FCC process may comprise particulate cracking catalyst and
33 the present NO_x reduction additive, each as separate
34 particles. The NO_x reduction additive is added to the
35 inventory of circulating particulate solids in an NO_x
36 reducing effective amount; that is, in an amount which is
37 effective for reducing the NO_x content in the regenerator

1 flue gas below that which would be present in the absence
2 of the additive. Preferably, the inventory of circulating
3 particulate solids contains from about 0.001 to about 10
4 percent by weight, and more preferably from about 0.01 to
5 about 5 percent by weight, and most preferably from about
6 0.05 to about 1 percent by weight of the NO_x reduction
7 additive.

8

9 When present as a separate particle, the NO_x reduction
10 additive particle may optionally include, in addition to
11 the spinel, perovskite and stabilization components
12 disclosed hereinbefore, at least one cracking component.
13 In this embodiment it is generally preferred that the
14 additive contain at most about 40 weight percent of at
15 least one cracking component. It is more preferred that
16 the additive contain at most about 25 weight percent, and
17 even more preferred that the additive contain from about 1
18 to about 25 weight percent of at least one cracking
19 component. Greater levels of the cracking component may
20 be preferred when the flue gas contains a low carbon
21 monoxide concentration. Catalytic materials known to have
22 cracking activity at the conditions of the FCC reactor are
23 suitable as cracking components in the present process.
24 Also suitable are catalytic materials which form a surface
25 coke layer while passing through the FCC reactor zone in
26 the presence of hydrocarbon reactants. These include, for
27 example, zeolite Y, rare earth exchanged zeolite Y,
28 ultrastable zeolite Y, calcium-exchanged zeolite Y, ZSM-5,
29 acid exchanged clay, and amorphous aluminosilicate. In
30 preparing the additive containing the cracking component,
31 it is preferred that the cracking component be added to
32 the gel containing the spinel precursor, or to the gel
33 solid containing spinel precursors and perovskite
34 precursors, prior to drying and calcining to form the
35 additive.

36

1 The additive, which may include the cracking component, is
2 added to the inventory of circulating particulate solids
3 in an NO_x reducing effective amount. In most cases, from
4 about 0.001 to about 10 weight percent of the additive
5 will be present, where the amount of the additive in the
6 inventory is computed on a cracking component free basis,
7 ie., from the sum of the weights of spinel, perovskite,
8 and stabilization components, if any, in the additive,
9 excluding the weight of the cracking component. It is
10 more preferred that the inventory contain from about 0.01
11 to about 5 weight percent, and still more preferred from
12 about 0.05 to about 1.0 weight percent of the NO_x
13 reduction additive, on a cracking component free basis.

14

15 The additive may be in any form suitable for circulation
16 in the circulating particulate solids inventory in the
17 cracking system. A major amount by weight of the additive
18 will typically have a diameter in the range from about 10
19 microns to about 250 microns, and preferably in the range
20 from about 60 microns to about 120 microns. The surface
21 area of the additive is typically in the range from about
22 25 m²/gm to about 600 m²/g.

23

24 While the NO_x reduction additive of the present invention
25 is active for reducing the NO_x content of FCC regenerator
26 flue gas, it has a negligible effect on the hydrocarbon
27 cracking reactions which occur during the FCC process.
28 Furthermore, the additive is compatible with CO oxidation
29 promoters which may be part of the inventory of
30 circulating particulate solids.

31

32 Reduction of NO_x in the FCC regenerator proceeds via a
33 reaction pathway involving reaction between a reducing
34 agent and the NO_x generated during combustion of nitrogen-
35 containing carbonaceous material on coked FCC catalyst.
36 One reducing agent useful in the present process is carbon
37 monoxide, which may be generated during combustion of the

1 carbonaceous material. It is important for the present
2 process that at least one mole of carbon monoxide be
3 available at the point of reaction of the NO_x for each
4 mole of NO_x to be reduced. Since the NO_x reduction
5 reaction is enhanced by additional carbon monoxide, CO/NO_x
6 molar ratios in the flue gas of greater than 2/1 are
7 preferred. As NO_x reduction activity is enhanced by
8 excess CO, CO/NO_x molar ratios of 500/1 or greater are
9 also within the scope of the present invention.

10

11 Carbon monoxide concentrations in the region of the
12 additive are affected by a number of factors, including
13 excess oxygen in the flue gas, availability and amount of
14 CO oxidation promoters in the FCC catalyst inventory,
15 temperature of the regenerator, the quality of catalyst
16 mixing in the regenerator catalyst bed and the amount of
17 oxidation gas bypass through the bed. Under conditions of
18 low flue gas CO concentrations, increasing the amount of
19 cracking component in the NO_x reduction additive provides
20 additional carbon monoxide which is available for NO_x
21 reduction without significantly increasing the overall
22 carbon monoxide produced in the FCC regenerator. Thus,
23 the present invention is efficient for reducing NO_x in
24 flue gas to very low levels, as low as 5 ppmv. Typical
25 flue gas NO_x concentrations are less than about 5000 ppmv
26 and more commonly range from about 50 ppmv to about 500
27 ppmv.

28

29 There is available to the refiner a number of known
30 methods for controlling the carbon monoxide content of the
31 flue gas at the desired level, including, for example, by
32 maintaining an amount of an oxidation promoter in the FCC
33 catalyst inventory. Platinum group metals, including
34 platinum, palladium, ruthenium, rhodium, iridium, and
35 osmium, are routinely used for this purpose. The amount
36 of oxidation promoter to be added for carbon monoxide
37 combustion in the regenerator in the practice of this

1 invention depends on many factors, including regenerator
2 temperature, type of feed to the FCC reactor, and the
3 configuration of the regenerator. In general, increased
4 amounts of oxidation promoter decrease the amount of
5 carbon monoxide and increase the amount of NO_x in the
6 regenerator flue gas. When platinum group metals are used
7 as carbon monoxide oxidation promoters in the practice of
8 this invention, the amount of platinum group metal
9 promoter may be as high as 10 ppm, based on the total
10 weight of FCC catalyst inventory. For optimum NO_x
11 control, it is preferred that the amount of platinum group
12 metal promoter be maintained at or below 1 ppm.

13

14 Likewise, increasing the amount of oxygen exiting with the
15 FCC regenerator flue gas tends to decrease the amount of
16 carbon monoxide available for reaction with the NO_x on the
17 additive. Excess oxygen also tends to increase the
18 production of NO_x in the regenerator flue gas. It is
19 therefore preferred that the oxygen content of the FCC
20 regenerator flue gas leaving the regenerator be less than
21 5%, and preferably less than 4% on a volume or molar
22 basis.

23

24 As discussed above, the NO_x reduction additive is stable
25 in the presence of high sulfur oxide concentrations in the
26 flue gas. Typical sulfur oxide concentrations range from
27 about 50 ppmv to about 5000 ppmv, though generally they
28 range from about 100 ppmv to about 1000 ppmv.

29

30 One skilled in the art of FCC processes will recognize
31 that while in the present process the NO_x reduction
32 additive reduces the NO_x content of the FCC regenerator
33 flue gas in the inventory of circulating particulate
34 solids within the regenerator, the composition of the flue
35 gas is generally determined at some location remote from
36 the inventory of circulating particulate solids, typically
37 in a flue gas transfer line or at a flue gas exhaust port

1 external to the regenerator. It will also be apparent to
2 one skilled in the art that the method selected for
3 determining the flue gas composition is not critical to
4 the present invention. NO_x content may be determined, for
5 example, using the wet chemical techniques and
6 spectroscopic methods described in 40 CFR Ch. 1 (7-1-91
7 Edition) Pt. 60, App. A. Method 7.

8

9 These and other specific applications of the process are
10 illustrated by the following examples.

11

12

EXAMPLES

13

14

Example 1

15

16 NO_x reduction additives of this invention were prepared as
17 follows:

18

19

Preparation of Additive 1:

20

21 A spinel support was prepared by dissolving 200 grams of
22 magnesium nitrate hexahydrate and 585 grams of aluminum
23 nitrate nonahydrate in 1000 ml water, and then adding this
24 solution to 750 ml of concentrated ammonium hydroxide
25 solution in 1500 ml water. The precipitate was then
26 filtered, washed, dried, and calcined at 700°C for 1 hr.
27 The calcined product was then ground and screened down to
28 the 45 to 150 μm range. The spinel had a surface area of
29 128 m^2/gm and a pore volume of 0.299 cc/gm.

30

31

32 16% LaCu_{0.4}Mn_{0.6}O₃ on spinel was prepared by impregnating the
33 spinel support with the appropriate quantities of the
34 corresponding metal salts, and then calcining the material
at 950°C for 30 min.

1 Preparation of Additive 2:

2
3 $\text{LaCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ was prepared in bulk by ball-milling the
4 appropriate quantities of lanthanum oxide, manganese
5 carbonate, and copper (II) oxide followed by a calcination
6 at 1100°C for 10 hours. The resulting black perovskite
7 powder was then ball milled.

8
9 4.0 grams of the finely ground $\text{LaCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ powder was then
10 suspended in a solution of 45 grams magnesium nitrate
11 hexahydrate and 132 grams aluminum nitrate hexahydrate
12 dissolved in 225 ml of water. This slurry was then added
13 to 170 ml of concentrated ammonium hydroxide in 340 ml of
14 water. The resulting precipitate/perovskite mixture was
15 then filtered, washed to remove the excess NH_3 and NH_4NO_3 ,
16 dried overnight at 100°C, calcined at 450°C for 1 hr and
17 then at 700°C for 1 hr. The resulting 16% $\text{LaCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ in
18 spinel additive was then ground and screened, and the
19 particles in the 40 to 150 μm range were recovered for
20 testing.

21
22 Preparation of Additive 3:

23
24 $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ (where Ln is a rare earth mixture containing
25 mainly La, Pr, and Nd and possibly Ce) was prepared by
26 ball milling 26.2 grams rare earth carbonate (Molycorp
27 5230), 2.58 grams CuO , and 5.60 grams MnCO_3 , and then
28 calcining the material at 700°C for 5 hours. X-ray
29 diffraction indicated that a $\text{LaCu}_x\text{Mn}_{1-x}\text{O}_3$ perovskite phase
30 had formed along with a small amount of $\text{Ce}_2\text{Nd}_2\text{O}_7$ contaminant
31 phase.

32
33 4 grams of the $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ was then slurried into 170 ml of
34 concentrated ammonium hydroxide in 340 ml of water using a
35 high shear mixer, and a solution of 45.0 grams of
36 magnesium nitrate hexahydrate and 131.8 grams of aluminum
37 nitrate nonahydrate dissolved in 225 ml of water was added

1 with continued mixing. The precipitate which formed was
2 filtered and dried at 100°C, calcined at 700°C, and
3 contained 16% by weight $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ in MgAl_2O_4 spinel. The
4 calcined product was ground and screened, and particles in
5 the 45 to 150 μm size range were recovered for catalytic
6 testing.

7

8 Preparation of Additive 4:

9

10 $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ was prepared in a manner analogous to Additive
11 3, except that the stoichiometry was corrected to account
12 for the formation of $\text{Ce}_2\text{Nd}_2\text{O}_7$. 8.3 grams of this $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$,
13 was dispersed with 7.1 grams of a "light" grade of MgO
14 into 125 ml of water using a high shear mixer. 18.0 grams
15 (on a dry basis) of a peptizable alumina which had been
16 peptized in a mixture of 200 ml of water and 4.1 ml of 88%
17 formic acid was blended in using a high shear mixer. The
18 resulting material, after being dried at 150°C, and
19 calcined at 700°C, contained 25% by weight $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ in
20 MgAl_2O_4 spinel. The calcined material was ground, and
21 particles in the 45 to 150 μm size range were recovered
22 for catalytic testing.

23

24 Preparation of Additive 5:

25

26 10 grams of Additive 4 was impregnated with 1.0 gram of
27 copper sulfate pentahydrate dissolved in 3 ml of water to
28 give additive 5 having 2.5% copper (on a metals weight
29 basis).

30

31 Preparation of Additive 6:

32

33 25% $\text{LnCu}_{0.2}\text{Mn}_{0.8}\text{O}_3$ in spinel was prepared in a manner
34 analogous to Additive 3 except that the stoichiometry of
35 $\text{LnCu}_{0.2}\text{Mn}_{0.8}\text{O}_3$ was corrected to account for the formation of
36 $\text{Ce}_2\text{Nd}_2\text{O}_7$.

37

1 Preparation of Additive 7:

3 10 grams of Additive 6 was impregnated with copper sulfate
4 pentahydrate in a manner analogous to example 24 to form
5 2.5% copper (on a metals basis) on 25% $\text{LnCu}_{0.2}\text{Mn}_{0.8}\text{O}_3$ in
6 spinel.

7

8 Preparation of Additive 8:

9

10 25% $\text{LnCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ in spinel was prepared in a manner
11 analogous to Additive 3 except that the stoichiometry of
12 $\text{LnCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ was corrected to account for the formation of
13 $\text{Ce}_2\text{Nd}_2\text{O}_7$.

14

15 Preparation of Additive 9:

16

17 $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ was again prepared in a manner analogous to
18 that of Additive 4, except that a cerium free version of
19 the rare earth carbonate (Molycorp 5231) was used.

20

21 In a manner analogous to that of Additive 4, a peptizable
22 alumina was gelled with formic acid and the appropriate
23 quantity of magnesium oxide was added to the gel. The
24 $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ and a USY zeolite (PQ 300-56) was slurried into
25 water before being added to the gel. After drying at
26 350°C and calcining at 700°C for 1 hr, the material was
27 ground and screened down to the 45 to 150 μm range to form
28 15% $\text{LnCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ /15% USY zeolite in MgAl_2O_4 .

29

Example 2

31

32

33 Comparative additives were prepared as follows:

34

35 Preparation of Comparative Additive 10:

36

1 26.52 grams of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 26.64 grams of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,
2 and 7.12 grams $\text{Cu}(\text{NO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ were dissolved in 10 ml of
3 water by warming the solution on a hot plate. This
4 solution was then dripped onto 100 grams of calcined Alcoa
5 C-30 alumina, which had been heated to 70°C. After
6 drying, the material was calcined at 950°C for 30 min. to
7 form an additive with a hypothetical stoichiometry of 16%
8 $\text{La}_{0.66}\text{Cu}_{0.33}\text{MnO}_3$ supported on alumina. X-ray diffraction
9 revealed that the sample was multi-phased, and contained
10 kappa alumina, a $\text{LaCu}_x\text{Mn}_{1-x}\text{O}_3$ perovskite, and a copper
11 manganese spinel with a stoichiometry of approximately
12 $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$.

13

14 Preparation of Comparative Additive 11:

15

16 $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ was prepared by grinding together the appropriate
17 quantities of copper oxide and manganese carbonate in a
18 ball mill, and then calcining the powder at 1100°C for 10
19 hours.

20

21 Preparation of Comparative Additive 12:

22

23 A spinel support was prepared by dissolving 200 grams of
24 magnesium nitrate hexahydrate and 585 grams of aluminum
25 nitrate nonahydrate in 1000 ml water, and adding this
26 solution to a second solution of 750 ml of concentrated
27 ammonium hydroxide in 1500 ml water. The precipitate was
28 then filtered, washed, dried, and calcined at 700°C for 1
29 hr. The calcined product was then ground and screened,
30 and particles in the 45 to 150 μm range recovered. The
31 spinel had a surface area of 128 m^2/gm and a pore volume of
32 0.299 cc/gm.

33

34 A perovskite with a hypothetical stoichiometry of 16%
35 $\text{La}_{0.66}\text{Cu}_{0.33}\text{MnO}_3$, on spinel was prepared by impregnating the
36 spinel support with the appropriate quantities of the
37 corresponding metal salts, and then calcining the material

1 at 950°C for 30 min. X-ray diffraction indicated the
2 presence of poorly crystalline magnesium aluminum spinel
3 along with a $\text{LaCu}_x\text{Mn}_{1-x}\text{O}_3$ perovskite type phase. The
4 presence of the copper manganese spinel could not be
5 ascertained because of the overlap of its peaks with the
6 magnesium aluminum spinel.

Example 3

The activities of the above additives of this invention and comparative additives were determined by measuring the percent NO_x reduction of a 130 ppm NO/490 ppm CO in nitrogen stream as it fluidized a 40 gram bed of unpromoted equilibrium catalyst containing 0.10 grams of the additive being tested. The equilibrium catalyst containing the additive was then aged a predetermined number of cycles in a fluidized bed reactor that was designed to simulate the FCC process. This aging unit was programmed to add a West Texas sour vacuum gas oil containing 1.02% S over a two minute period to the fluidized bed at 1000°F. On a total weight basis the catalyst to oil ratio equaled 11. The equilibrium catalyst containing the NO_x additive was then stripped at 1000°F with a mixture of 90% steam/10% nitrogen for three minutes, followed by a regeneration step using air containing 10% steam at 1300°F for 5 minutes. The total cycle time was 14 minutes. Following a predetermined number of cycles, the catalyst was then placed back in the NO tester to determine its new activity. The results are shown in Table I.

31
32 The following observations can be drawn from the results
33 shown in Table I. Additives containing oxides having
34 perovskite structures and oxides having spinel structures
35 have better long-term activity than do those additives
36 having perovskite structures in combination with non-
37 spinel oxides such as alumina. Adding copper to the

1 perovskite/spinel oxides further improves the long-term
2 activity. Conversely, preparing the perovskite with
3 excess transition metal, as in Additive 12, causes
4 undesirable phases to form, which results in decreased
5 long-term activity of the additive.

6

7 There are numerous variations on the above examples which
8 are possible in light of the teachings supporting the
9 present invention. It is therefore understood that within
10 the scope of the following claims, the invention may be
11 practiced otherwise than as specifically described or
12 exemplified herein.

13

1
2

TABLE I

3
4
5
6
7

Additive	% NO Reduction		
	Fresh Additive Activity	Aged Additive	
		No. of Cycles	Activity
Additives of this Invention			
1	46	46	76
		160	35
2	28	200	31
3	49	200	23
		400	17
4	48	140	33
5	50	200	64
		300	50
6	64	200	10
7	69	185	71
8	40	200	12
9	34	187	29
Comparative Additives			
11	0		
10	43	50	5
12	60	45	4

25

1 WHAT IS CLAIMED IS:

2

3 1. A process for reducing the NO_x content of an FCC
4 regenerator flue gas comprising contacting said flue gas
5 at FCC regeneration conditions with an NO_x reducing
6 effective amount of an additive comprising:

7

8 (a) a perovskite containing at least one transition
9 metal;

10

11 (b) a spinel containing at least one Group IIA element
12 and at least one Group IIIA element; and

13

14 (c) at most about 10 weight percent of a stabilization
15 component comprising an element or compound thereof
16 selected from the group consisting of copper, zinc
17 and mixtures thereof.

18

19 2. The process according to Claim 1 wherein the transition
20 metal is selected from the group consisting of chromium,
21 manganese, iron, cobalt, nickel, copper, and zinc.

22

23 3. The process according to Claim 1 wherein the perovskite
24 further comprises at least one component selected from
25 the group consisting of Group IA, Group IIA, and Group
26 IIIB elements.

27

28 4. The process according to Claim 2 wherein the perovskite
29 further comprises a rare earth element.

30

31 5. The process according to Claim 4 wherein the perovskite
32 has the general formula LnCu_xMn_{1-x}O₃, where "Ln" represents
33 at least one element selected from the group consisting

1 of lanthanum, cerium, neodymium, and praseodymium, and
2 wherein "x" has a value of at most about 0.6.

3

4

5 6. The process according to Claim 1 wherein the additive
6 contains from about 1 to about 40 percent by weight of
7 the perovskite.

8

9 7. The process according to Claim 6 wherein the additive
10 contains from about 5 to about 35 percent by weight of
11 the perovskite.

12

13 8. The process according to Claim 1 wherein the spinel is a
14 magnesia alumina spinel.

15

16 9. The process according to Claim 1 wherein the additive
17 contains between about 0.1 and about 5 weight percent of
18 the stabilization component.

19

20 10. The process according to Claim 1 wherein the additive
21 further comprises a cracking component.

22

23 11. The process according to Claim 10 wherein the cracking
24 component is selected from the group consisting of
25 zeolite Y, rare earth exchanged zeolite Y, ultrastable
26 zeolite Y, calcium-exchanged zeolite Y, ZSM-5, acid
27 exchanged clay, and amorphous aluminosilicate.

28

29 12. The process according to Claim 11 wherein the cracking
30 component is zeolite Y.

31

32 13. The process according to Claim 10 wherein the additive
33 comprises at most about 40 weight percent of the cracking
34 component.

35

1 14. The process according to Claim 13 wherein the additive
2 contains at most about 25 weight percent of the cracking
3 component.

4

5 15. A process for reducing the NO_x content of FCC regenerator
6 flue gas, said process comprising cracking hydrocarbons
7 in the absence of externally supplied molecular hydrogen
8 in a cracking system employing an inventory of
9 circulating particulate solids including cracking
10 catalyst particles, said inventory being cycled between a
11 cracking zone and a catalyst regeneration zone, wherein
12 said hydrocarbons are cracked in contact with said
13 catalyst particles and coke is formed on said catalyst
14 particles at cracking conditions in said cracking zone,
15 and flue gas is formed by burning said coke off said
16 catalyst particles with oxygen or a molecular oxygen-
17 containing gas at regeneration conditions in said
18 regeneration zone, and said flue gas is vented from said
19 regeneration zone, wherein said process comprises adding
20 to said inventory of circulating particulate solids an
21 NO_x reducing effective amount of an additive comprising:
22

23

24 (a) from about 10 to about 30 weight percent of a
25 perovskite having the general formula $LnCu_xMn_{1-x}O_3$,
26 where "Ln" represents at least one element selected
27 from the group consisting of lanthanum, cerium,
28 neodymium, and praseodymium, and wherein "x" has a
29 value of at most about 0.6;

30

31 (b) from about 0.5 to about 5 weight percent of a
32 stabilization component comprising an element or
33 compound thereof selected from the group consisting
34 of copper, zinc and mixtures thereof; and

1 (c) a magnesia alumina spinel to make 100 weight percent.

2

3 16. The process according to Claim 15 wherein the additive

4 further comprises a cracking component.

5

6 17. The process according to Claim 16 wherein the additive

7 further comprises at most about 40 weight percent of the

8 cracking component.

9

10 18. The process according to Claim 16 wherein the cracking

11 component is selected from the group consisting of

12 zeolite Y, rare earth exchanged zeolite Y, ultrastable

13 zeolite Y, calcium-exchanged zeolite Y, ZSM-5, acid

14 exchanged clay, and amorphous aluminosilicate.

15

16 19. The process according to Claim 15 wherein said inventory

17 of circulating particulate solids contains from about

18 0.001 to about 10 weight percent of the NO_x reduction

19 additive, on a cracking component free basis.

20

21 20. The process according to Claim 15 wherein said vented

22 regenerator flue gas contains less than about 5000 ppmv

23 NO_x.

24

25 21. The process according to Claim 15 wherein said vented

26 regenerator flue gas contains less than about 500 ppmv

27 NO_x.

28

29 22. The process according to Claim 15 wherein said vented

30 regenerator flue gas contains at most about 5 percent by

31 volume molecular oxygen.

32

33 23. The process according to Claim 15 wherein said vented

34 regenerator flue gas contains from about 50 ppm to about

35 5000 ppmv of sulfur oxides.

1 24. An NO_x reduction additive comprising:

2

3 (a) from about 1 to about 40 weight percent of a
4 perovskite having the general formula $LnCu_xMn_{1-x}O_3$,
5 where "Ln" represents at least one element selected
6 from the group consisting of lanthanum, cerium,
7 neodymium, and praseodymium, and wherein "x" has a
8 value of at most about 0.6;

9

10 (b) at most about 10 weight percent of a stabilization
11 component comprising an element or compound thereof
12 selected from the group consisting of copper, zinc
13 and mixtures thereof; and

14

15 (c) a magnesia alumina spinel to make 100 weight percent.

16

17 25. The process according to Claim 24 wherein the additive
18 contains from about 5 to about 35 weight percent of the
19 perovskite.

20

21 26. The process according to Claim 24 wherein the additive
22 contains from about 10 to about 30 weight percent of the
23 perovskite.

24

25 27. The process according to Claim 24 wherein the additive
26 further comprises a cracking component.

27

28 28. The process according to Claim 27 wherein the additive
29 further comprises at most about 40 weight percent of the
30 cracking component.

31

32 29. The process according to Claim 27 wherein the additive
33 comprises at most about 25 weight percent of the cracking
34 component.

- 1 30. The process according to Claim 27 wherein the cracking
2 component is selected from the group consisting of
3 zeolite Y, rare earth exchanged zeolite Y, ultrastable
4 zeolite Y, calcium-exchanged zeolite Y, ZSM-5, acid
5 exchanged clay, and amorphous aluminosilicate.
- 6
- 7 31. The process according to Claim 30 wherein the cracking
8 component is zeolite Y.
- 9
- 10 32. A cracking catalyst composition comprising a particulate
11 cracking catalyst and from about 0.001 to about 10 weight
12 percent, on a cracking component free basis, of an NO_x
13 reduction additive, said additive comprising:
14
- 15 (a) from about 1 to about 40 weight percent of a
16 perovskite having the general formula $LnCu_xMn_{1-x}O_3$,
17 where "Ln" represents at least one element selected
18 from the group consisting of lanthanum, cerium,
19 neodymium, and praseodymium, and wherein "x" has a
20 value of at most about 0.6;
- 21
- 22 (b) at most about 10 weight percent of a stabilization
23 component comprising an element or compound thereof
24 selected from the group consisting of copper, zinc
25 and mixtures thereof; and
- 26
- 27 (c) a magnesia alumina spinel to make 100 weight percent.
- 28
- 29 33. The composition according to Claim 32 wherein said
30 additive further comprises at most about 40 weight
31 percent of a cracking component.
- 32

1 34. The composition according to Claim 32 wherein the
2 cracking catalyst composition contains from about 0.01 to
3 about 5 percent by weight of the additive.

4

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/06655

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C10G11/05; C10G11/04; B01D53/36

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols		
Int.C1. 5	C10G	;	B01D ; B01J

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,5 037 538 (MOBIL OIL) 6 August 1991 cited in the application ---	
A	EP,A,0 318 808 (KATALISTIKS INTERNATIONAL) 7 June 1989 ---	
A	WO,A,8 905 186 (ASEA BROWN BOVERY) 15 June 1989 ---	
A	DATABASE WPI Week 9145, Derwent Publications Ltd., London, GB; AN 91-329749 & JP,A,3 221 125 (TOYOTA JIDOSHA) 24 January 1990 see abstract ---	-/-

¹⁰ Special categories of cited documents :¹¹ "A" document defining the general state of the art which is not considered to be of particular relevance¹² "E" earlier document but published on or after the international filing date¹³ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)¹⁴ "O" document referring to an oral disclosure, use, exhibition or other means¹⁵ "P" document published prior to the international filing date but later than the priority date claimed¹⁶ "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹⁷ "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹⁸ "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art¹⁹ "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

07 OCTOBER 1993

Date of Mailing of this International Search Report

18.10.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

MICHIELS P.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 455 491 (SAKAI CHEMICAL INDUSTRY) 6 November 1991 ---	
A	EP,A,0 468 127 (PEKING UNIVERSITY) 29 January 1992 -----	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9306655
SA 76700

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 07/10/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5037538	06-08-91	None		
EP-A-0318808	07-06-89	US-A- 4957718 AU-A- 2581988 JP-A- 1236297 JP-B- 5000432		18-09-90 01-06-89 21-09-89 05-01-93
WO-A-8905186	15-06-89	DE-A- 3741888 EP-A- 0344306 JP-T- 2502444 US-A- 5093301		22-06-89 06-12-89 09-08-90 03-03-92
EP-A-0455491	06-11-91	JP-A- 4016238 JP-A- 4027437 JP-A- 4027428 JP-A- 4027429 JP-A- 4027435 JP-A- 4027431 JP-A- 4029747 JP-A- 4029743		21-01-92 30-01-92 30-01-92 30-01-92 30-01-92 30-01-92 31-01-92 31-01-92
EP-A-0468127	29-01-92	CN-A- 1058357 AU-B- 634028 AU-A- 7138391 US-A- 5242881		05-02-92 11-02-93 30-01-92 07-09-93